Development of a Novel Gas Pressurized Stripping (GPS)-Based Technology for CO₂ Capture from Post-Combustion Flue Gases DE-FE0007567

Project Kick-Off Meeting

Carbon Capture Scientific, LLC.
CONSOL Energy Inc.
Nexant Inc.

Pittsburgh, PA November 8, 2011



Presentation Outline

- **☐** Project Overview
- □ Technology Fundamentals and Background
- ☐ Scope of Work
- □ Technical Approach
- □ Project Management



Project Objectives

- □ Perform bench-scale tests of individual process units to obtain necessary process design data for the pilot scale
- □ Conduct computer simulations to maximize the benefit of the GPS technology for existing power plants
- □ Carry out experimental investigation of selected solvents to minimize the economic risk of the GPS technology.

Project Team and Focus

DOE/NETL

COR- Timothy Fout

Carbon Capture Scientific, LLC

- Computer simulation to optimize GPS based process for existing power plants
- Bench-scale experiments to obtain process design data for GPS based process

CONSOL Energy Inc.

Work with CCS to acquire phase equilibrium and related process design data

Nexant Inc.

Conduct techno-economic analyses for the GPS based technology

Project Team- Key Personnel

■ NETL Timothy E. Fout (COR)

□CCS Shiaoguo (Scott) Chen (PI)

Zijiang (John) Pan (Co-PI)

Kevin C. O'Brien (Project manager)

Zhiwei (David) Li (Task leader)

Technician A (Laboratory specialist)

□CONSOL Energy Inc.

Daniel P. Connell (Co-PI)

Mark Dunkerley (Co-PI)

Richard Winchel (Technical advisor)

■Nexant Inc.

Gerald Choi (PI)

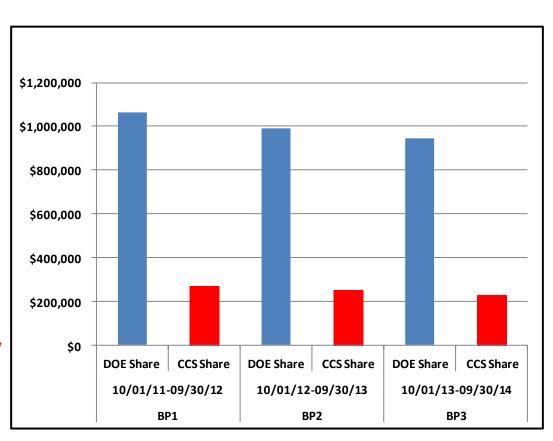
Robert Chu (Sr. Chemical Engineer)

Project Budget

Project duration: 10/1/2011 - 9/30/2014

	Budget, \$
DOE	2,999,756
ccs	751,178*
Total	3,750,934

*including \$84,605 from CONSOL Energy (Cost share is ~20%)



DOE funding and cost share on a yearly basis

Presentation Outline

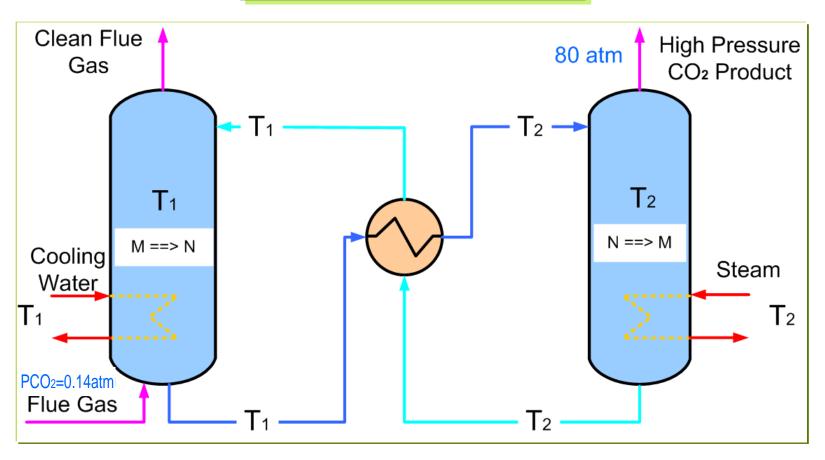
- **☐** Project Overview
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Thermodynamics of the Post-Combustion CO₂ Capture Processes

- A generic CO₂ capture/regeneration process
- Minimum heat requirement of the generic process
- Electricity equivalent of the minimum heat
- Limitations of amine as absorption/stripping solvents
- Repeated generic CO₂ capture processes
- Thermodynamics of repeated generic processes

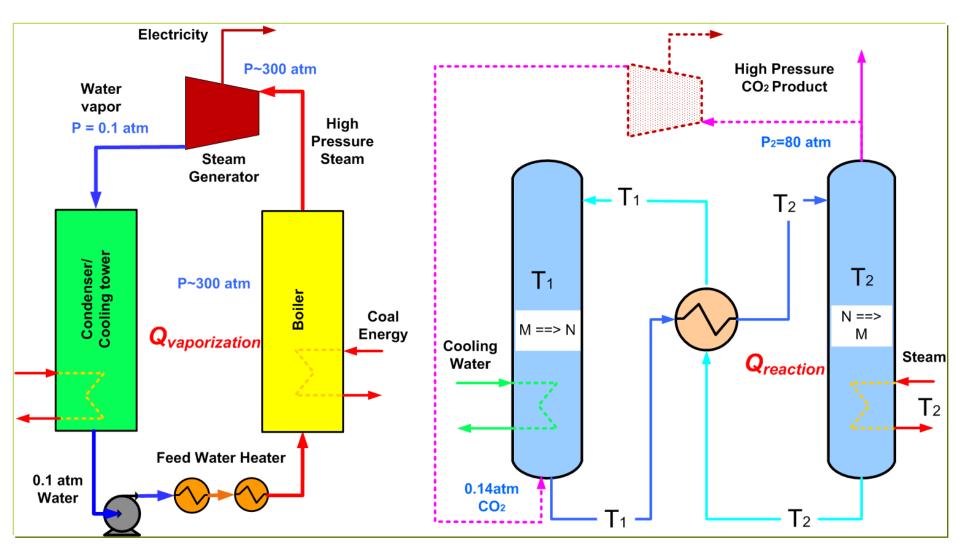
A Generic Process for CO₂ Capture from Post-Combustion Flue Gases

$$M + CO_2 \longrightarrow N + \Delta H$$



Ignore all the driving force for heat transfer

Analogy between Power Generation and CO₂ Capture from Flue Gas



Capture /Regeneration Operating Parameters

- Heat of Reaction
- CO₂ Capture temperature
- Regeneration temperature
- □ CO₂ partial pressure at capture
- □ CO₂ partial pressure at regeneration
- □ CO₂ recovery rate

- $= \Delta H (kJ/kgCO_2)$
- $= T_1 = 313 (K)$
- $= T_2 = ? (K)$
- $= P_1 = 0.14$ (atm.)
- $= P_2 = 80$ (atm.)
- = 90%

Minimum Heat Requirement of the Generic CO₂ Capture Process

CO₂ Capture/ Regeneration:

$$M + CO_2 \Leftrightarrow N + \Delta H$$

Equilibrium constant expression:

solid:
$$K = \frac{1}{P_{CO2}}$$

Ideal solution:
$$K = \left(\frac{x_N}{x_M}\right) \frac{1}{P_{CO2}}$$

Non ideal liquid:
$$K = \left(\frac{\gamma_N x_N}{\gamma_M x_M}\right) \frac{1}{P_{CO2}}$$

And the equation correlates K and T is so called Van't Hoff equation:

$$\frac{d \ln K}{dT} = \frac{\Delta H}{RT^2}$$

Minimum Heat Requirement of the Generic CO₂ Capture Process

For non ideal liquid solvents:

$$\frac{d \ln K}{dT} = \frac{\partial \ln \gamma_N + \partial \ln x_N - \partial \ln \gamma_M - \partial \ln x_M - \partial \ln P_{CO2}}{\partial T}$$

$$= \frac{\partial \ln \gamma_N - \partial \ln \gamma_M - \partial \ln P_{CO2}}{\partial T} \approx -\frac{\partial \ln P_{CO2}}{\partial T} = -\frac{\Delta H}{RT^2}$$

The relationship between activity coefficient and temperature is:

$$\frac{d \ln \gamma_i}{dT} = -\frac{\Delta \overline{H}_i}{RT^2}$$

 ΔH_i is partial molar heat of mixing for component i, usually it is much smaller than heat of reaction

Minimum Heat Requirement of the Generic CO₂ <u>Capture Process</u>

Ignore activity coefficient change with temperature, above equation can be integrated:

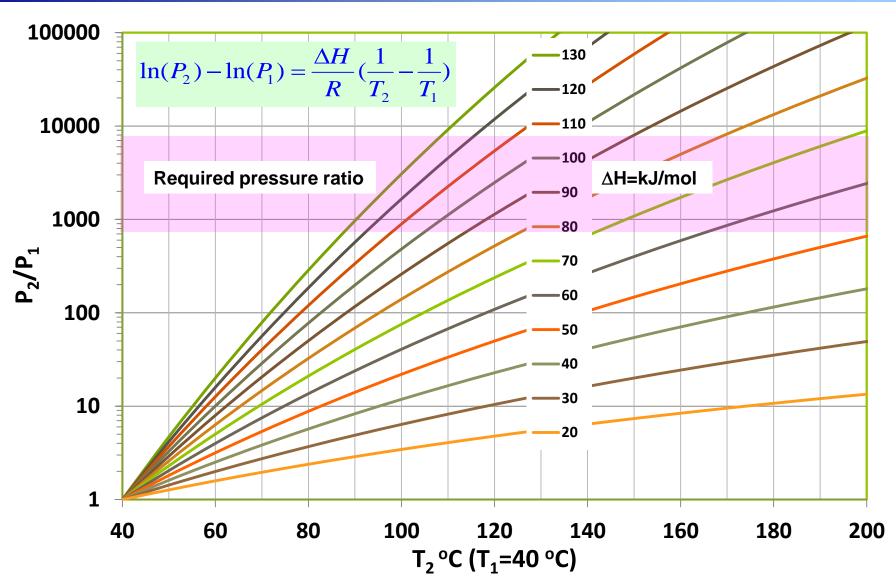
$$\ln(P_2) - \ln(P_1) = \frac{\Delta H}{R} \left(\frac{1}{T_2} - \frac{1}{T_1} \right)$$

And rearrange above, we have:

$$\Delta H = -R[\ln(P_2) - \ln(P_1)] \frac{T_1 T_2}{T_2 - T_1}$$

Minimum heat requirement can be calculated for different temperature swing ranges and different pressure requirement

Minimum Heat Requirement



Electricity Equivalent of the Minimum Heat

Minimum heat:

$$\Delta H = -R[\ln(P_2) - \ln(P_1)] \frac{T_1 T_2}{T_2 - T_1}$$

And the Carnot Efficiency of the ΔH at T₂ is:

$$\eta_{carnot} = (1 - T_1/T_2)$$

Thus the electricity equivalent is:

$$W = (\Delta H) * \eta_{carnot} = R[\ln(P_2) - \ln(P_1)] \frac{T_1 T_2}{T_2 - T_1} \times (1 - T_1/T_2)$$
$$= RT_1(\ln(P_2) - \ln(P_1)) = RT_1 \ln(P_2/P_1)$$

Idel gas:
$$W_{comp} = -\int_{v_1}^{v_2} P \ dv = -\int_{v_1}^{v_2} \frac{RT_1}{v} \ dv = RT_1 ln \frac{P_2}{P_1}$$

Electricity Equivalent of the Minimum Heat -- Case of Post-Combustion with 90% Removal

Post-Combustion CO₂ capture with 90% removal:

$$P_1$$
= 0.014~0.14atm (90% of CO_2 removal)
 P_2 =80 atm

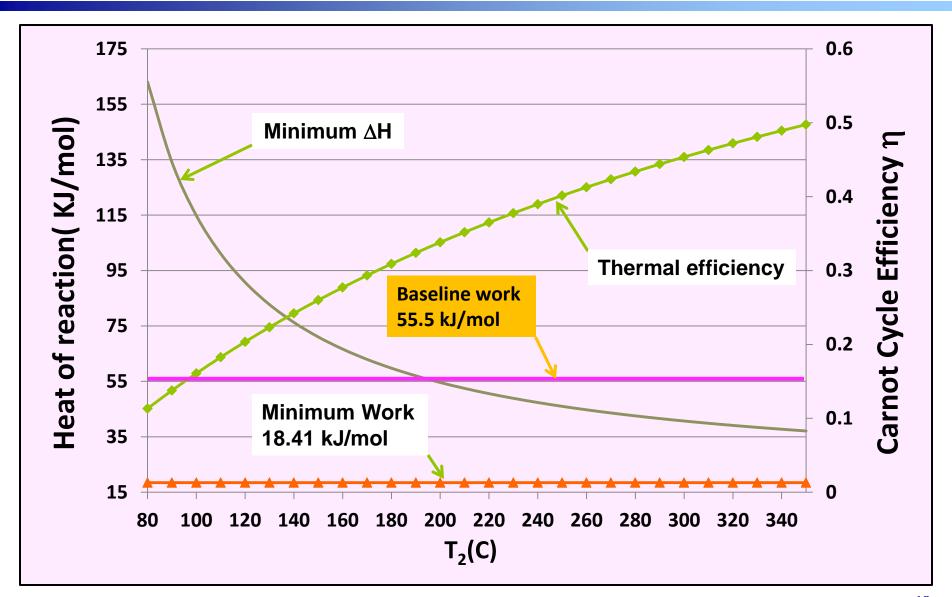
$$W = (\Delta H) * \eta_{carnot} = RT_1[\ln(P_2) - \ln(P_1)]$$

At 90% removal P_1 changes from P_a =0.014 to P_b =0.14 atm and the average minimum work is:

$$W = RT_1(\ln P_2 - P_b \ln P_b + P_a \ln P_a + (P_b - P_a))/(P_b - P_a))$$

= 18.41(kJ/mol) = 0.116 (kWh/kgCO₂)

Minimum Heat, Thermal Efficiency and Minimum Work



Limitations of Amine As Absorption/Stripping Solvent

CO₂ conditions for post combustion flue gas:

Initial P: $P_1 = 0.014 \sim 0.14$ atm

Product P: P₂=80 atm

(90% of CO₂ removal)

Absorption T: $T_1=313K$

Stripping T: T_2 =393K

Required heat of reaction:

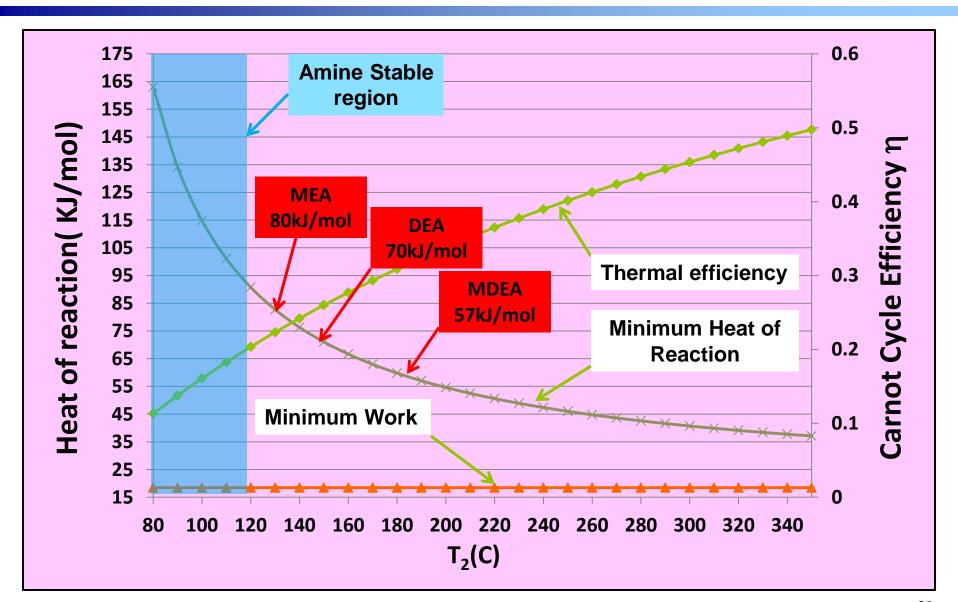
$$\Delta H = -R[\ln(P_2) - \ln(P_1)] \frac{T_1 T_2}{T_2 - T_1}$$

$$= 12.571 \times [\ln(80) - \ln(P_1)] = 55.88 - 12.571 \ln(P_1)$$

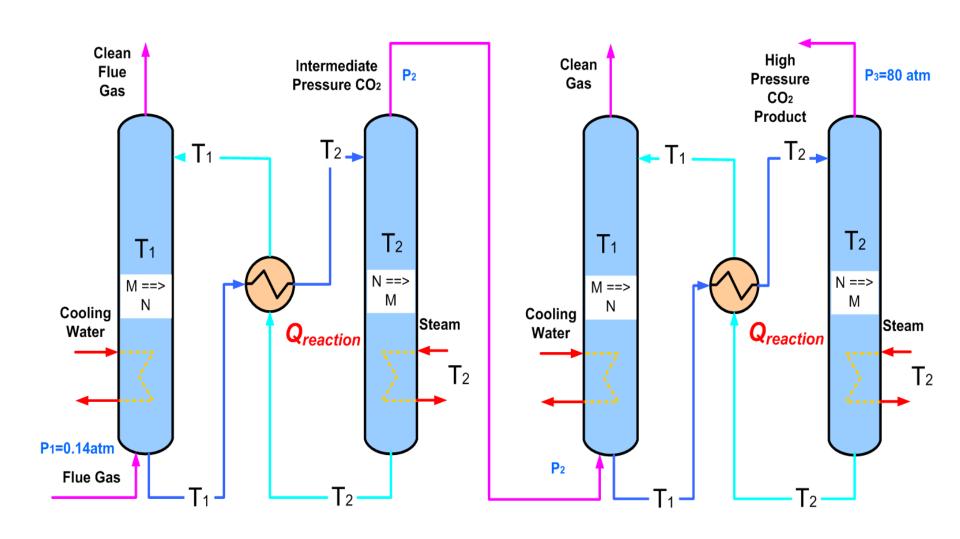
 P_1 changes from P_a =0.014 atm to P_b =0.14 atm; by integrating above equation between P_a and P_b , we have:

$$\Delta H = 55.88 - 12.571(P_b \ln(P_b) - P_a \ln(P_a) - (P_b - P_a)) / (P_b - P_a)$$
$$= 90.44(kJ / molCO_2) = 2055(kJ / kgCO_2)$$

Limitations of Amine As Absorption/Stripping Solvent



Repeated CO₂ Absorption/Stripping Process



Thermodynamics of the Repeated Generic Process

Repeated absorption/stripping cycles between the same temperature range (e.g. 40 - 120 °C):

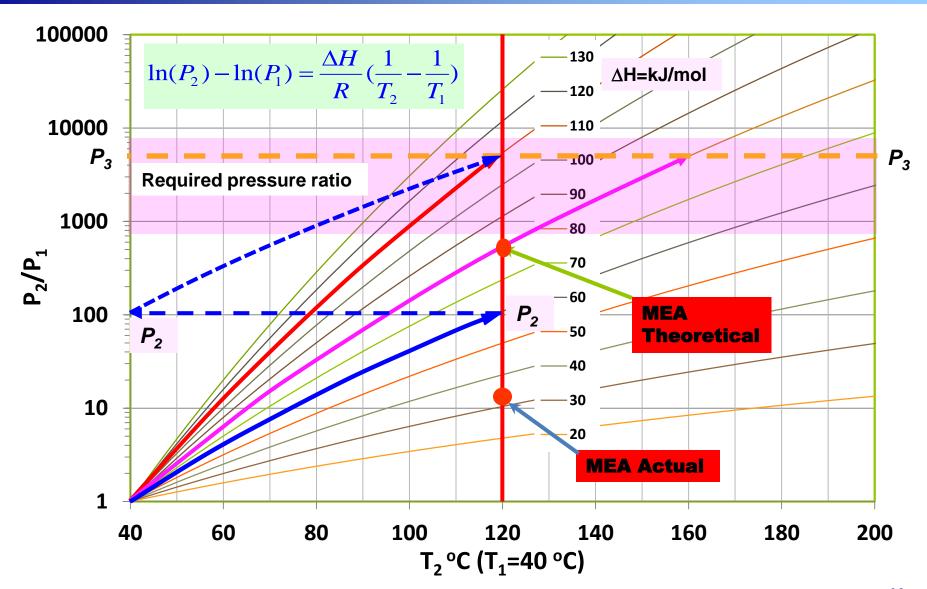
$$\ln(P_2) - \ln(P_1) = \frac{\Delta H_1}{R} (\frac{1}{T_2} - \frac{1}{T_1})$$

$$\ln(P_3) - \ln(P_2) = \frac{\Delta H_2}{R} \left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

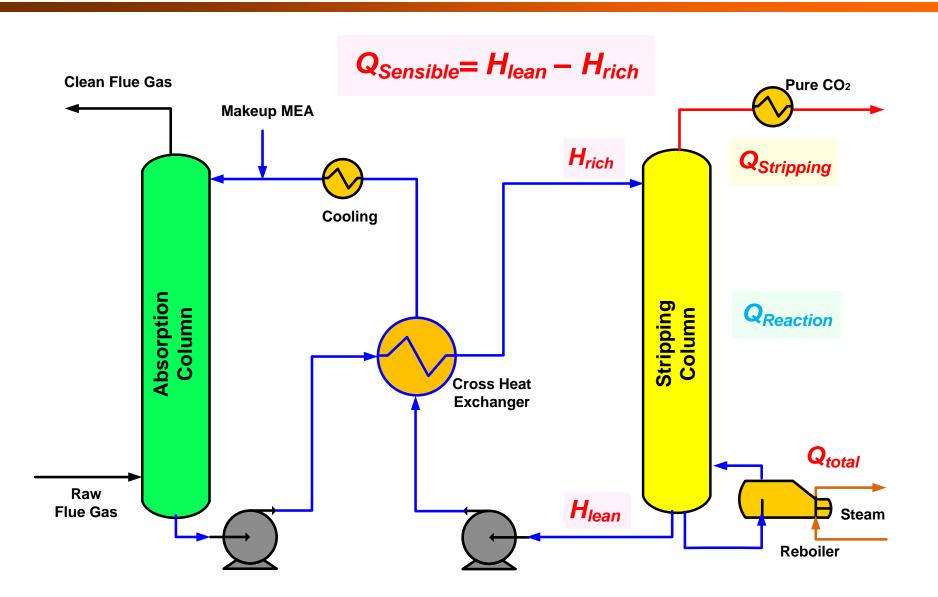
Combining the two cycles:

$$\ln(P_3) - \ln(P_1) = \frac{\Delta H_1 + \Delta H_2}{R} (\frac{1}{T_2} - \frac{1}{T_1})$$

Thermodynamics of the Repeated Generic Process



Conventional Amine-Based Absorption/Stripping Processes



Heat Components of the Conventional Process

$$Q_{total} = Q_{sensible} + Q_{reaction} + Q_{stripping}$$

$$Q_{sensible} = \frac{C_p(T_{lean hot} - T_{rich hot})}{\Delta Loading}$$

$$Q_{reaction} = \Delta H_{reaction}$$

$$Q_{stripping} = \left(\frac{P_{H_2O}}{P_{CO_2}}\right)_{\substack{Top \ of \\ the \\ stripper}} \Delta H_{H_2O}$$

Issues with Conventional Strippers

Water vapor is used as stripping gas

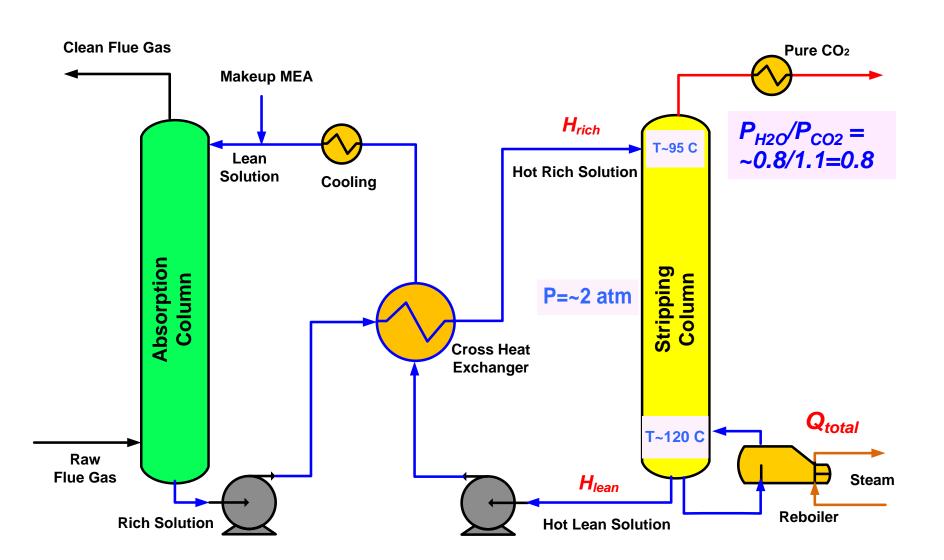
Low operating pressure

Water vapor is also used as a heat carrier

Consequences:

- -Low thermal efficiency
- High compression work

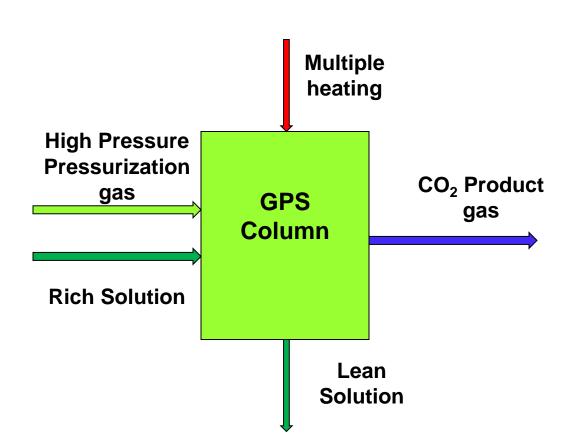
Conventional Amine-Based Absorption/Stripping Processes



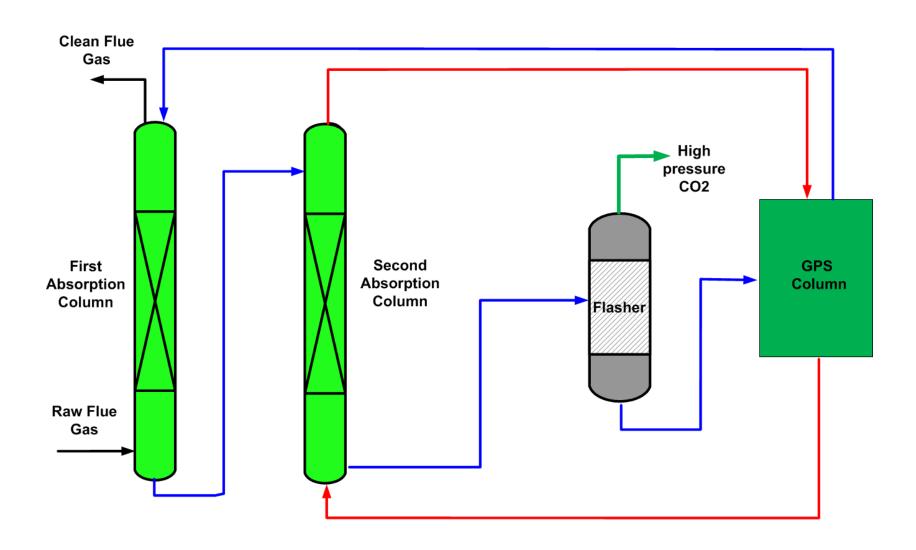
The Novel Gas Pressurized Stripping (GPS) Column

Using a high pressure gas to create high pressure CO₂

Introducing multiple heaters



Novel GPS Based Absorption/Stripping Process



Advantages of the GPS Based Processes

- Uses on-the shelf technology
 - Most suitable for large scale applications such as power plants
- ☐ High operating pressure
 - Low stripping heat
- ☐ Minimal or no need for mechanical CO₂ compression
 - Uses thermal compression
 - High thermal efficiency (low exergy loss)
- **☐** Flexible
 - Many common units with the conventional absorption/stripping processes
 - Can be repeatedly used depending on the needs
- ☐ Second absorption step can reduce oxidative degradation
 - Second absorber is a stripper for absorbed oxygen

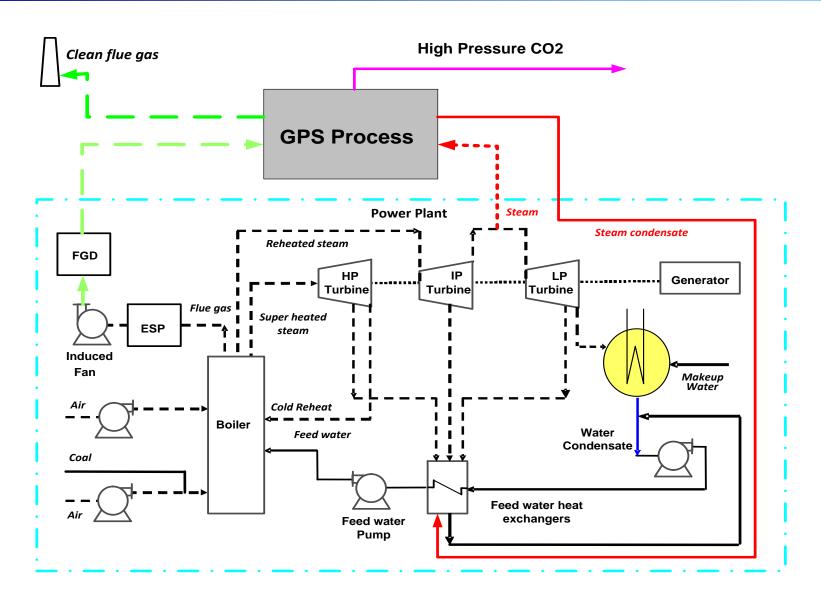
Comparison of Heat Usage for Conventional and GPS Processes

	Conventional Process	GPS Process
$Q_{sensible}$	$\frac{C_p(T_{leanhot} - T_{richhot})}{\Delta Loading}$	$\frac{C_p(T_{leanhot} - T_{richhot})}{\Delta Loading}$
Qreaction	ΔH_1	$\Delta H_1 + \Delta H_2$
Qstripping	$\left(rac{P_{H_2O}}{P_{CO_2}} ight)_{egin{subarray}{c} At \ top \ of \ the \ stripper \ \end{array}} \Delta H_{H_2O}$	$ \left\{ \left(\frac{P_{H_2O}}{P_{CO_2}} \right)_{\substack{Top \ of \\ the \ GPS \\ stripper}} + \left(\frac{P_{H_2O}}{P_{CO_2}} \right)_{\substack{At \ the \\ flashers}} \right\} \Delta H_{H_2O} $

Preliminary Computer Simulation Results of the GPS Process

Process	Current MEA	GPS Process
First Reaction Heat MJ/kgCO ₂	1875	2550
Second Reaction Heat MJ/kgCO ₂	0	
Sensible Heat MJ/kgCO ₂	1150	425
Stripping Heat MJ/kgCO ₂	850	220
Total Heat MJ/kgCO ₂	3875	3195
Compression Work kWh/kgCO ₂	0.1	0.017
Electricity Equivalent kWh/kgCO ₂	0.30	0.18

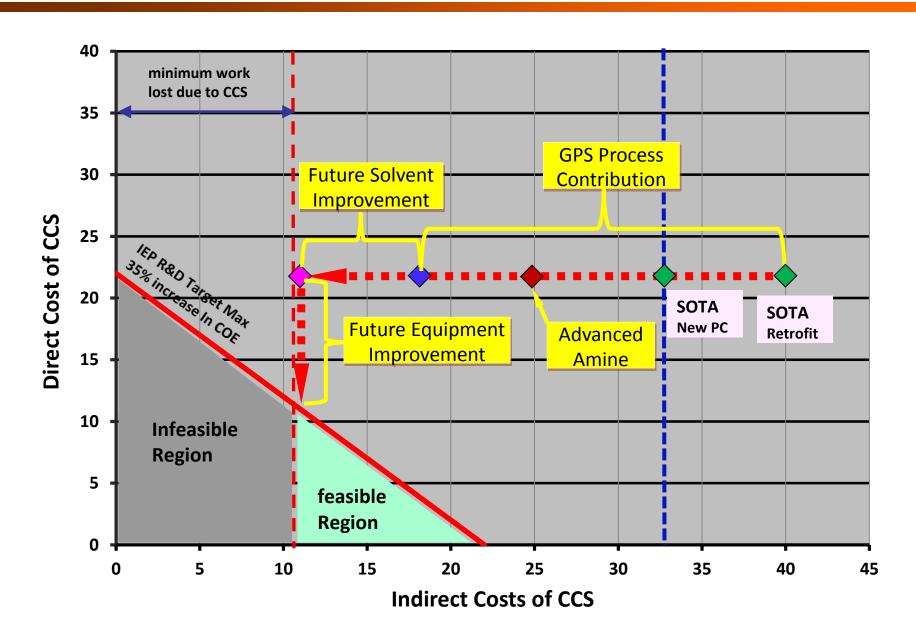
Integration of a GPS process with an existing power plant



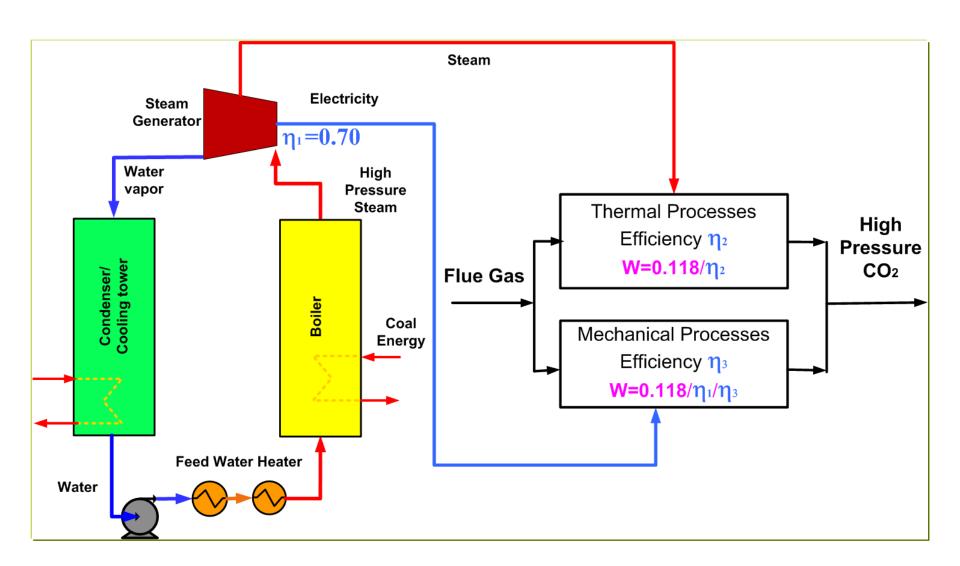
Achieving DOE's Techno-economic Goals

- □ <u>Direct Costs</u>: capital and operating costs associated with capture, transport, and sequestration of CO₂
- Indirect Costs: costs of modification of existing plant AND other costs associated with de-rating the plant
- Indirect costs dominate over direct costs

Goal Diagram for EPEC CCS Incremental Mills/kWh



Comparison between mechanical and thermal processes



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Scope of Work

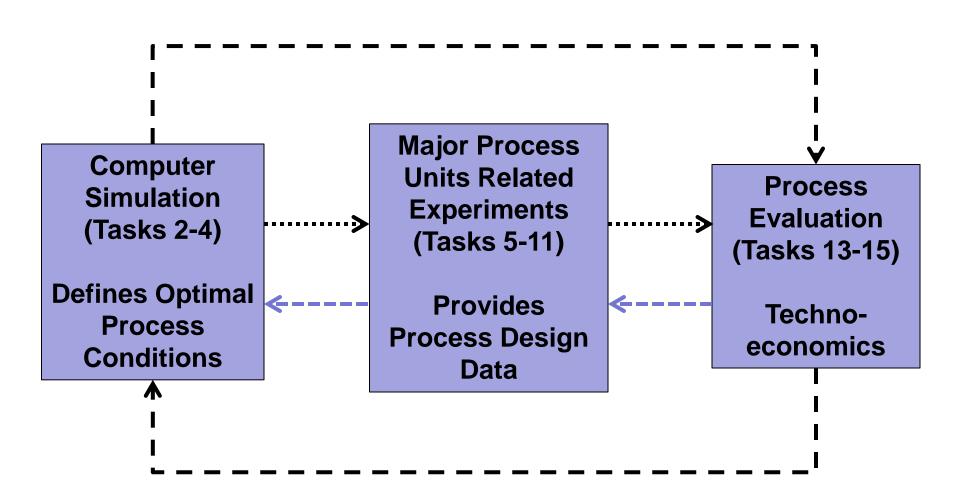
Combine experimental, modeling/process simulation, and techno-economic analysis studies to develop and evaluate the GPS technology

- Carbon Capture Scientific, LLC
 - Kinetics and thermodynamics tests using Individual process units
 - First and second absorber design
 - GPS column design
 - Flashers design
- CONSOL Energy Inc.
 - Solvent data and assistance in column design / testing
 - Phase Equilibrium data for selected solvent at high CO₂ loading and high temp
 - Heat capacity and viscosity of selected solvent
 - Column design / testing assistance
- Nexant Inc.
 - Systems analysis and preliminary techno-economic evaluation

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Technical Approach to Optimize & Iterate to Achieve DOE Goals



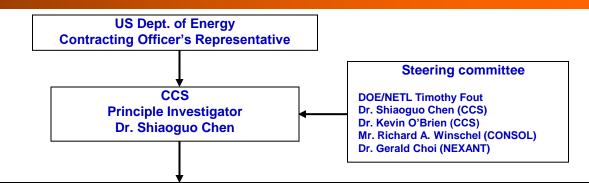
Tasks Designed to Utilize Unique Strengths of Organizations

Task	Description	Туре	Focus	CCS	CONSOL	Nexant
1	Project planning & management	n/a	PM	Χ		
2	Optimization of GPS process	Computer Simulation	Process	Χ		
3	Optimization of GPS process for existing plant	Computer Simulation	Process	Χ		
4	Optimization of flasher operating conditions	Computer Simulation	Process	Χ		
5	Data measurement at high loading and high Temp	Process Related Experiments	Solvent		χ	
6	First absorption column testing	Process Related Experiments	Process	Χ	χ	
7	GPS column design/fabrication and testing	Process Related Experiments	Process	Χ	χ	
8	Second absorption column testing	Process Related Experiments	Process	Χ	χ	
9	Stability of solvent at high loading and Temp	Process Related Experiments	Solvent	Χ		
10	Corrosion test at high loading and Temp	Process Related Experiments	Solvent	Χ		
11	Physical properties measurement	Process Related Experiments	Solvent		χ	
12	Survey of EH&S of GPS process	Process Related Experiments	Solvent	Χ		
13	Preliminary techno-economic analysis	Process Evaluation	Economics			χ
14	Revising of techno-economic analysis	Process Evaluation	Economics			Χ
15	Updated techno-economic analysis	Process Evaluation	Economics			Χ

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- Project Management

Project Organization



Task 1. Planning
Management & Reporting
CCS leads
Dr. Kevin O'Brien
(CCS, 2100 hours)
Dr. Shiaoguo Chen
(CCS, 760 hours)

Task 2. GPS column study and its optimization CCS leads Dr. Zhiwei Li (CCS, 920 hour) Dr. Shiaoguo Chen (CCS, 104 hours) Task 3. Optimization of GPS process for existing plant CCS leads Dr. Zhiwei Li (CCS, 920 hour) Dr. Shiaoguo Chen (CCS, 112 hours)

Task 4.
Optimization of flasher operating conditions
CCS leads
Dr. Zhiwei Li
(CCS, 920 hour)
Dr. Shiaoguo Chen
(CCS, 112 hours)

Task 5. Measurement of phase equilibrium data at high loading and high T CONSOL leads
Mr. Daniel Connell (CONSOL, 255 hours)
Dr. Shiaoguo Chen (CCS, 300 hours)

Task 6. First absorption column testing CCS leads Dr. Shiaoguo Chen (CCS, 276 hours) Dr. Zijiang Pan (CCS, 200 hour) Mr. Dunkerley (CONSOL, 85 hour)

Task 8. Second absorption
column testing
CCS leads
Dr. Shiaoguo Chen
(CCS, 128 hours)
Dr. Zijiang Pan
(CCS, 265 hour)
Mr. Daniel Connell (CONSOL,
272 hours)

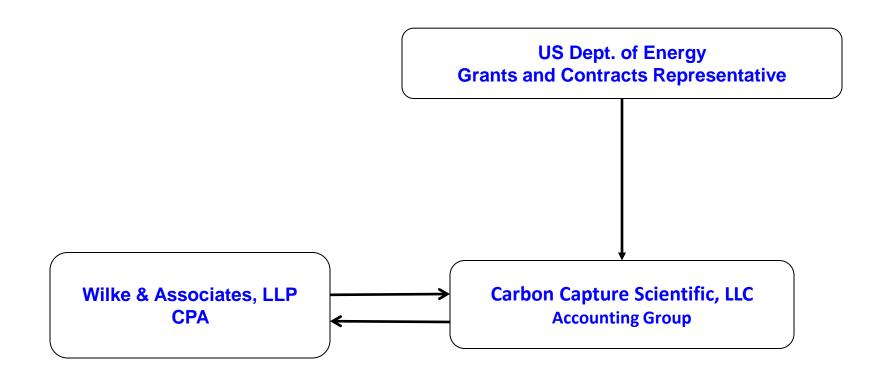
Task 9. Stability of solvent at high loading and high T CCS leads Dr. Shiaoguo Chen (CCS, 200 hours) Dr. Zijiang Pan (CCS, 600 hours)

Task 10. Corrosion test at high loading and high T CCS leads Dr. Shiaoguo Chen (CCS, 200 hours) Dr. Zijiang Pan (CCS, 600 hours)

Task 11. Physical properties measurement CCS leads
Dr. Shiaoguo Chen (CCS, 200 hours) (CCS, 600 hours)
Mr. Dunkerley
CONSOL, 352 Hours

Task 12. Survey of EH&S of GPS process CCS leads Dr. Shiaoguo Chen (CCS, 146 hours) Dr. Zhiwei Li (CCS, 330 hours) Task 13. Preliminary technoeconomic analysis
Nexant leads
Dr. Gerald Choi
(Nexant, 140 hours)
Mr. Robert Chu
(Nexant, 160 hours) Task 14. Revision of technoeconomic analysis Nexant leads Dr. Gerald Choi (Nexant, 50 hours) Mr. Robert Chu (Nexant, 160 hours) Task 15. Updated technoeconomic analysis Nexant leads Dr. Gerald Choi (Nexant, 100 hours) Mr. Robert Chu (Nexant, 115 hours)

Financial Program Management



Project Schedule: Oct.1, 2011 – Sept.30, 2014

2.1 GPS column performance study 2.2 GPS column performance study 3.1 Impact of absorption temperature on energy use 3.3 Impact of absorption temperature on energy use 3.4 Impact of absorption temperature on energy use 3.5 Impact of absorption temperature on energy use 3.5 Impact of absorption temperature on energy use 4.1 GPS based CO ₂ compression 4.1 GPS based CO ₃ compression 4.1 Superficient system of the superficient of the substance of the superficient of the substance of the superficient of the substance of th																																					
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Project Milestone Log

А	GPS column study and optimization to achieve thermal efficiency of 60% or greater
В	Solvent loss due to degradation of solvent is less than 3 kg/ton CO ₂
С	Overall energy performance column and solvent less than or equal to 0.22 kwh/kg CO ₂
D	GPS column efficiency experimental measured at 50% or greater
Е	Overall energy performance of system less than or equal to 0.20 kwh/kgCO ₂
F	Increase in capital equipment costs of less than or equal to 20% over existing process

Success Criteria / Decision Points / Actions to be Taken

Success Criteria	Decision Point / Actions
Solvent Loss due to degradation < 3 kg/ ton CO ₂	 Loss due to degradation >3 kg/ ton CO₂ Lower operating temperatures in the GPS column and flashers Change solvent concentration
Techno-economics Capital cost of GPS process < 20% increase over conventional amine process	 Capital cost of GPS process > 20% increase over those for conventional amine-based processes Modify operating conditions of some critical units Example: higher operating pressure for GPS columns and flashers may improve thermodynamic efficiency of the process, but could impact capital cost
Process Energy Consumption (including compression) < 0.22kWh/kgCO ₂	 Total energy consumption (including compression) > 0.22kWh/kgCO₂, Review simulation and experimental results Additional process optimization studies performed to identify and resolve problems

Mitigating Technical Risks

Description of Risk	Probability (L,M,H)	Impact (L,M,H)	Risk Management (Mitigation and Response Strategies)
Technical Risks:			
			First, the operating temperature of the flashers will be lowered so that loss will be reduced to an acceptable level
<u>SOLVENT</u> Stability Issues	М	L	2. Second, if the first step is not enough, the operating temperature of the GPS column will be reduced so that solvent loss will be reduced to an acceptable level
			Amine stabilization chemicals will be added if possible
SOLVENT Excessive Corrosion	L	L	 Construction materials of the flashers with more resistance to corrosion will be selected. Corrosion inhibitors will be added to
			the system to prevent the corrosion
SOLVENT Foaming	M	L	Anti-foaming chemicals will be added to the system
ECONOMICS Not achieving targets	L	Н	 Identify the process units which are critical to the process economics Analyze the issues related to the high capital cost
SOLVENT Environmental, health and safety (EH&S) issues	L	L	 Identify the issues and propose mitigation pathways Change solvent formulation Replace with a better solvent

Project Deliverables

- Project Management Plan
- Quarterly progressive reports
- Annual DOE contractors meeting
- ☐ Final technical report
 - Summary of all development, analysis, testing, design, and economic analysis
- Other reports
 - Financial, property, annual renewal, and close-out reporting, as defined in contract

Acknowledgements

☐ U.S. Department of Energy/ National Energy Technology Laboratory under Agreement No. DE-FE0007657



Questions/ Comments?



Minimum Work of CO₂ Capture --- Continued

B. Minimum Work of CO₂ Compression (from 1 atm):

$$W_{\min,comp} = \Delta H - T\Delta S$$

Т	Р	Н	S	W _{min,comp}	RT $\ln(P_2/P_1)$
(C)	(atm)	(kJ/mol)	(J/mol*K)	(kJ/mol)	(kJ/mol)
40	1	22.828	122.3	0	0
40	20	22.066	95.654	7.58	7.80
40	40	21.101	87.59	9.14	9.60
40	80	17.543	72.305	10.37	11.40
40	150	12.543	54.737	10.87	13.04

C. Overall Minimum Work:

$$W_{\min} = W_{\min,sep} + W_{\min,comp} = 8.36 + 10.37 = 18.73(kJ/molCO_2)$$
$$= 425.7(kJ/kgCO_2) = 0.118(kWh/kgCO_2)$$

Minimum Work of CO₂ Capture --- Continued

